

THE INFLUENCE OF STERIC POTENTIAL ON THE PRESSURE AND INTERPARTICLE CORRELATIONS IN MAGNETIC FLUIDS

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In the present paper, we analyze the influence of the steric potential on the interparticle correlation in magnetic fluids. Using molecular dynamics simulations and diagram technique, we obtain the radial distribution function for a monodisperse system of soft-dipolar spheres. On the basis of the pair correlation function we compute the pressure associated with the presence of dipolar particles in magnetic fluids. Comparing our findings to the results obtained for dipolar hard spheres it is shown that the steric potential plays a very important role for pressure and should be accurately taken into account.

Introduction. Magnetic fluids are stable suspensions of single domain magnetic particles [1]. The ability to combine liquid state and strong magnetic response makes magnetic fluids very attractive for various medical [2] and technological [3] applications. All applications of magnetic fluids are based on the profound understanding of the relation between the magnetic fluid microstructure and its macroscopic properties. That is why numerous theoretical, simulation and experimental studies of ferrofluid microstructure, rheology, scattering properties, etc. (see, e.g., [4]–[6] and references therein) have been performed in recent 40 years.

In all those studies, interparticle interactions were shown to play a crucial role in the analysis of the ferrofluid behaviour. Here, we would like to understand what kind of contribution magnetic and various steric interactions can make to the particle-related part of pressure in magnetic colloids. For that purpose, two different methods are employed: analytical calculations and molecular dynamics simulations.

The present paper is organized in the following way: in section 1, the model of magnetic fluids under investigation is described. The next section 2 is devoted to the proposed methods for analytical calculation of pressure using a diagram technique and to details of computer simulation performance. Results and discussions are presented in section 3. Conclusions on the work are presented in section 4.

1. The model. The system under investigation is a bulk monodisperse magnetic fluid (ferrofluid), which consists of spherical magnetic dipolar particles with a diameter σ . Each particle has a magnetic moment μ . The interactions between particles in such a system are described by a combination of two potentials. The first one is the dipole-dipole potential:

$$U_{dd}(i, j) = \frac{\mu_0}{4\pi} \left[\frac{\langle \mu_i, \mu_j \rangle}{|\mathbf{r}_{ij}|^3} - 3 \frac{\langle \mu_i, \mathbf{r}_{ij} \rangle \langle \mu_j, \mathbf{r}_{ij} \rangle}{|\mathbf{r}_{ij}|^5} \right], \quad (1)$$

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where μ_i and μ_j are the particles' magnetic moments, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ is a displacement vector, and μ_0 is the vacuum permeability. The intensity of the dipole-dipole interaction is determined by a characteristic parameter $\lambda = \mu_0 \mu^2 / (4\pi \sigma^3 kT)$, which is the ratio of the dipole-dipole interaction at close contact of two particles to their thermal energy when the magnetic moments are in the so-called "head-tail" position. Here and further, k is the Boltzmann constant, and T is the temperature of the system.

The presence of non-magnetic layers on the particles' surface introduces steric repulsion between them, which is described either by the Weeks-Chandler-Anderson potential [7] given by Eq. (2) or by the hard-sphere potential

$$U_{\text{WCA}}(i, j) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma_i + \sigma_j}{2r_{ij}} \right)^{12} - \left(\frac{\sigma_i + \sigma_j}{2r_{ij}} \right)^6 \right] + \varepsilon, & r_{ij} < r_c \\ 0, & r_{ij} \geq r_c, \end{cases} \quad (2)$$

where $r_c = 2^{1/6}\sigma$ is a value of cutoff. This potential is a repulsive part of the Lennard-Jones potential, which is truncated at r_c and shifted by the depth of the potential wall ε . The hard-sphere potential, being very convenient for the analytical description of magnetic fluid properties, is widely used because of its simple form:

$$U_{\text{HS}}(i, j) = \begin{cases} \infty, & r_{ij} \leq \sigma \\ 0, & r_{ij} > \sigma. \end{cases} \quad (3)$$

In order to analyze the influence of the steric potential on the macroscopic parameters in magnetic fluids, we consider both hard- and soft-sphere potentials. We study the systems for a wide range of parameters: the particle density ρ varies from 0.5% to 10% with the step $\delta\rho = 0.005$, and the dipole-dipole interaction intensity λ is from 0.7 to 4.0 with the step $\delta\lambda = 0.3$. The methods used to calculate the pressure in the aforementioned model ferrofluids are presented in the next section.

2. Methods. For analytical calculation of the interparticle correlations in magnetic fluids, one might analyze the radial distribution function [8, 9, 11]. In general, the radial distribution function $g(r)$ can be presented in power series of the particle density [11]:

$$g(r) = \sum_{k=2}^{\infty} \rho^{k-2} B_k(r), \quad (4)$$

where the functions $B_k(r)$ have a structure similar to the one of the virial coefficients [11]. Each coefficient describes the contribution of interparticle correlations of a certain number of particles. In the present study, only two- and three-particle correlation are taken into account, which means that the radial distribution function is expanded up to the first order of density. Hence, the second and the third coefficients have the following form for any particles

$$B_2(r) = \langle f(1, 2) + 1 \rangle_{1,2}, \quad (5)$$

$$B_3(r) = \frac{1}{v} \int d\mathbf{r}_3 \langle (f(1, 2) + 1) f(2, 3) f(1, 3) \rangle_{1,2,3}, \quad (6)$$

where v is the particle volume, $f(i, j) = \exp\{-\beta U_{\text{dd}}(i, j) - \beta U_s(i, j)\} - 1$ is the Mayer function [12]. Here, the subscripts 1, 2 and 3 denote the numbers of three arbitrary chosen particles. In the formulas, averaging is performed over all positions of the particle centers and over all orientations of their magnetic moments.

To calculate the virial coefficients, the diagram approach was applied, which was also used in [8, 10]. According to this approach, the dipolar contribution to the Mayer function in (5) and (6) needs to be expanded as a series of the intensity of the dipole-dipole interaction λ . Thus, the radial distribution function for the monodisperse ferrofluid is presented in the following form

$$g(r) = \sum_{k=0}^{\infty} \sum_{n=0}^{\infty} \rho^k \lambda^n B_{kn}(r). \quad (7)$$

Each term of the series corresponds to the contribution of a certain diagram (see [8]) and is represented as a multi-dimension integral, which was calculated for magnetic fluids with soft-sphere repulsion. Here, all coefficients of the type B_{0n} define the contribution of the pure steric repulsion to the radial distribution function. Note that exact expressions for the functions B_{kn} of low orders for a system with hard sphere repulsion are already obtained and can be found in [8, 10].

Derivation of the radial distribution function (7) as a series of density and λ makes it possible to obtain the pressure using the following formula [11]

$$P = \rho kT - \frac{1}{6} \rho^2 \int \frac{d[U_{dd}(r) + U_s(r)]}{dr} g(r) r dr. \quad (8)$$

To verify our theoretical results, we perform molecular dynamics computer simulations using the simulation package ESPResSo [13]. The modelling system is composed of 512 spherical particles of reduced diameter $\sigma = 1$. Each particle has a reduced magnetic moment, the value of which corresponds to the aforementioned values of λ . Interactions of the particles are represented by the dipole-dipole potential (1) and Weeks–Chandler–Anderson potential (2). The particles are put into a cubic simulation box and infinitely replicated in 3D. To compute the long-range dipole-dipole interaction between all particles, a dipolar-P3M method was used [14]. The system was first equilibrated. During the next 30000 steps, statistics for the pressure and radial distribution functions was collected. Series of simulations were performed for each density in the range from 0.5% to 10%, which is mentioned above.

The next section discusses the results of analytical calculations for the pressure and radial distribution functions for a magnetic fluid with both soft-sphere and hard-sphere repulsion. The two theoretical models and obtained simulation data are compared there.

3. Results and discussions. The radial distribution function (RDF) allows to get information about the structural properties of the system. In order to compare the behaviour of the RDF for two different steric potentials, we plot these functions for a system of magnetic particles with soft-sphere and hard-sphere repulsions (see Fig. 1). The red lines in this figure correspond to the RDF for a system with hard-sphere repulsion, and the blue lines depict the RDF for a system with soft-sphere repulsion at $\lambda = 1.9$ at the particle low density $\rho = 0.01$ (Fig. 1a) and at the highest one $\rho = 0.1$ (Fig. 1b). All these curves have a very pronounced first peak. However, the height of this peak in case of soft-sphere repulsion is lower, and the peak itself is wider than that for a system with hard-sphere repulsion. Besides, the RDF for the system with soft-sphere repulsion shows that the particle centers can be located at a distance less than the diameter of a particle. The comparison of the RDFs suggests that the particle-related part of the pressure in magnetic fluids should be different for soft- and hard-sphere models. Later we will discuss how these differences in the RDF affect the pressure behaviour for systems of magnetic fluids with hard- and soft-sphere repulsion.

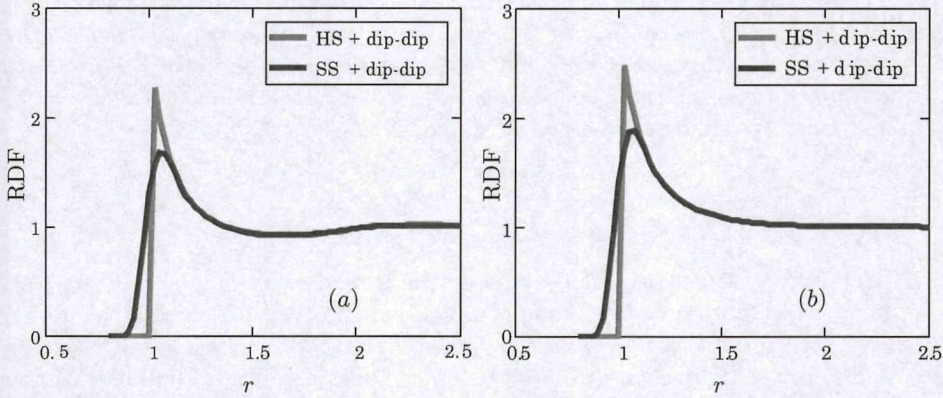


Fig. 1. The radial distribution function of magnetic fluids at $\lambda = 1.9$ with hard-sphere steric repulsion (HS) and with soft-sphere steric repulsion (SS) at the lowest density $\rho = 0.01$ (a) and at the highest density $\rho = 0.1$ (b).

Using the analytically obtained RDF, we calculated the pressure for magnetic fluids with the soft-sphere repulsion. The results of these calculations and the simulation data are presented in Fig. 2, which shows the pressure as a function of the dipole-dipole interaction intensity λ . Here, solid lines are theoretical predictions and the rhombuses are simulation data.

Is it clearly seen that they are in good agreement when both the density and the parameter λ are low. The reason for this is that, with the theoretical

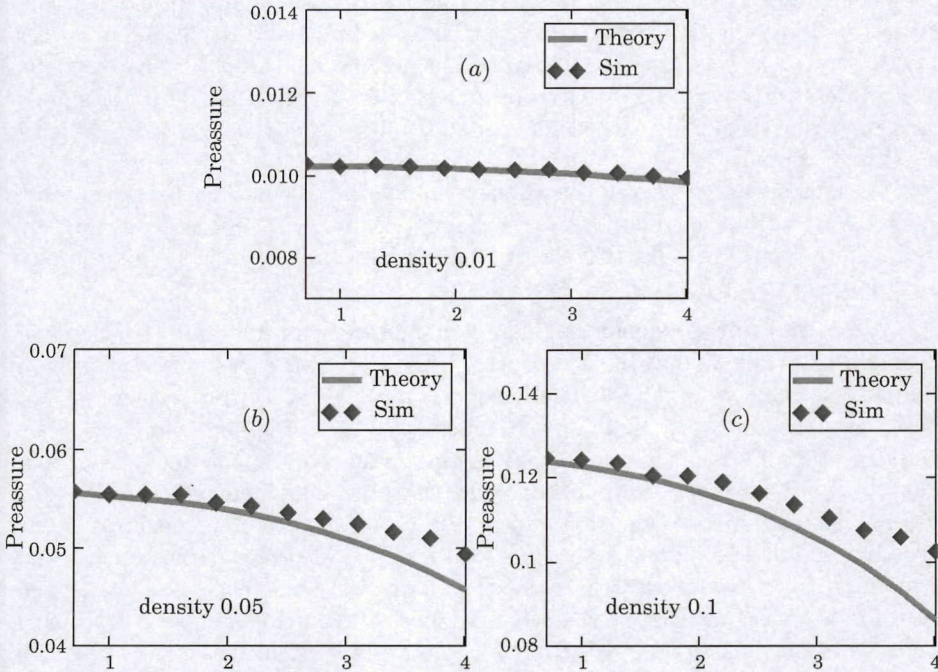


Fig. 2. Pressure as a function of intensity of the dipole-dipole interaction for a magnetic fluid with soft-sphere repulsion: (a) at the lowest density $\rho = 0.01$, (b) at the average density $\rho = 0.05$, and (c) at the highest density $\rho = 0.1$. Solid lines are theoretical predictions and points are the simulation data.

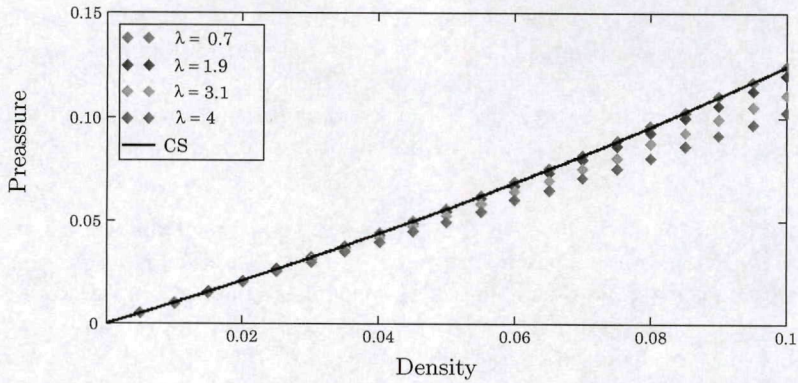


Fig. 3. Pressure as a function of density for a magnetic fluid with soft-sphere repulsion at different intensities of the dipole-dipole interaction λ . The black solid line denotes the pressure of a pure soft-sphere system without the dipole-dipole interaction.

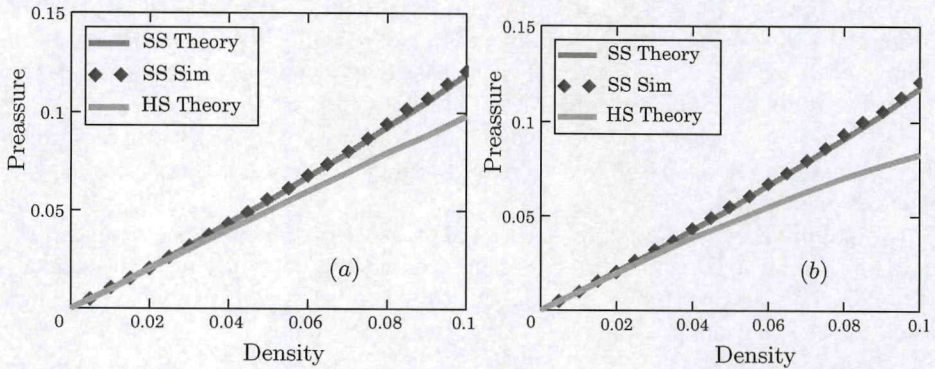


Fig. 4. Pressure as a function of density for a magnetic fluid with different types of repulsion at (a) $\lambda = 1.5$ and (b) $\lambda = 1.9$.

approach, only two- and three-particle correlations are taken into account when calculating the pressure, whereas the computer simulations allow to compute all interparticle correlations. The disagreement grows with the increase of λ . This suggests a hypothesis that the pressure is rather sensitive to the intensity of the dipole-dipole interaction. To verify this assumption, we plot only the simulation data for pressure as a function of density at different λ in a range from 0.7 to 4.0, which are presented as sets of colored rhombuses. Obviously, the pressure has to grow with the increasing density, as demonstrated in Fig. 3 for a systems of magnetic particles. These graphs show the inverse dependence of the pressure on the parameter λ : the increasing intensity of the dipole-dipole interaction leads to a noticeable pressure decrease. As to the influence of the dipole-dipole correlations on the pressure, here we also plot the pressure for a system with pure soft-sphere repulsion ($\lambda = 0$), which corresponds to the black curve in Fig. 3. This curve matches the data for the pressure at $\lambda = 0.7$ and all other curves lay below. Thus, the weak dipole-dipole interaction almost does not influence the pressure, which behaves as the one for a pure soft-sphere system, whereas the intense dipole-dipole interaction significantly decreases the pressure of the magnetic fluids.

Finally, we plot the pressure as a function of density at $\lambda = 1.5$ and $\lambda = 1.9$ when our theory (red solid line) is in agreement with the simulations (rhombuses), which are presented in Fig. 4a and Fig. 4b, respectively. These results were compared to the results for a system of magnetic particles with hard-sphere repulsion (green solid lines in these graphs) thoroughly investigated in [15]. It is clearly

seen that the green lines coincide with the results for the system with soft-sphere repulsion only at low densities. Thus, for the real system pressure calculations, one has to be accurate when choosing the steric potential for system modelling. In other words, one might need to allow for the soft-sphere repulsion despite the fact that the operation with the hard-sphere potential is much easier for theoretical methods.

4. Conclusion. In the present study, we analytically calculated the radial distribution functions for a system of dipolar soft spheres as a series of density and intensity of the dipole-dipole interaction using a diagram expansion technique. Using the expression for the RDF, we also calculated the pressure for this system. In order to elucidate deeper the influence of the dipole-dipole interaction on the particle-related contribution to the pressure of magnetic fluids, we performed molecular dynamics simulations and extensively compared the results with the theoretical predictions.

We showed that similarly to the dipolar hard spheres, the first-order density expansion of the radial distribution function made it possible to describe the behaviour of dipolar soft spheres for low values of λ only. However, the range of validity of this theoretical approach for the case of soft spheres is broader than the one of the dipolar-hard spheres [15].

We also found that for higher values of the dipolar strength the pressure of the system of dipolar soft spheres decreased, but the decrease was less pronounced than the one shown in [15].

To summarize, we investigated the influence of the short-range repulsion on the pair correlation functions and pressure and showed that the accurate consideration of the steric potential might be crucial when interpreting the experimental results on the thermodynamic properties of magnetic fluids.

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